EXTRA-FRAMEWORK ALUMINIUM IN THERMALLY TREATED ZEOLITE CaA

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Nuclear magnetic resonance spectra of aluminium including magic-angle spinning (27Al MAS NMR) have been measured in order to study the dealumination which is caused by a heat treatment of zeolite CaA. The extra-lattice aluminium exists partly in the form of Al(OH)₄⁻ anions, corresponding to at most about 17% of lattice dealumination.

1. Introduction

One interesting effect which accompanies a hydrothermal treatment of zeolites is the dealumination of the zeolite framework [1]. The value of the Si/Al ratio for the zeolite framework and its change can be determined by a measurement of the ²⁹Si or ²⁷Al nuclear magnetic resonance spectra with magic-angle spinning (MAS NMR) of the sample [2–6].

The concentration of even small amounts of extra-lattice aluminium which exists in the zeolite cages in a cubic symmetry can be determined directly from the ²⁷Al MAS NMR spectra. However, if the extra-lattice aluminium forms species of non-cubic symmetry, an ²⁷Al MAS NMR signal cannot be observed because of the strong line broadening by the quadrupole interaction. The concentration of this type of extra-lattice aluminium can be determined indirectly by comparing the concentration of the sum of lattice aluminium and of extra-lattice aluminium in a cubic symmetry, derived from the ²⁷Al MAS NMR spectra, with the total concentration of aluminium given by a chemical analysis.

With increasing temperature $T_a$ in a deep-bed activation procedure (cf. section 2) the total amount of extra-lattice aluminium of zeolites HY increases from about 20% to about 85% going from $T_a = 300^\circ$C to $600^\circ$C [4]. For $T_a = 300^\circ$C most of the extra-lattice aluminium species can be converted into Al(H₂O)₆³⁺ complexes by a rehydration of the samples. This latter complex gives rise to an ²⁷Al MAS NMR signal at 0 ppm. Its intensity decreases with increasing values of $T_a$, which has been explained by a condensation of the extra-lattice aluminium [4].

Extra-lattice aluminium exists also in zeolites of type CaA and other zeolites A exchanged with bivalent cations after a sample activation, as was shown for the first time by X-ray diffraction measurements [7]. Although the average concentration of aluminium released from framework positions is only small, it seems possible that an inhomogeneous distribution with enhanced values at the outer surfaces of crystallites may cause a barrier for molecular diffusion as described in ref. [8].

In the present paper ²⁷Al MAS NMR spectra were measured and analyzed in order to study the formation of extra-lattice aluminium accompanying deep-bed and shallow-bed activation of zeolite CaA.

2. Experimental

The basic material of all samples is Zeosorb 5AZ, a zeolite Ca₄₂Na₃₆A, purchased from VEB Chemiekombinat Bitterfeld. One portion of the samples was prepared under “deep-bed” (DB) conditions: About
1 g of zeolite was heated in an open glass tube (diameter 10 mm) under atmospheric pressure by raising the temperature at a rate of 100 K/h up to the chosen temperature of activation. After keeping the sample at this temperature for an additional 2 h, the sample was evacuated for 20 h. During this procedure the pressure decreased below 10 mPa. When the layer of the zeolite powder is less than 3 mm and the sample is heated in vacuo at a rate of 10 K/h up to the final (activation) temperature, the specimen is called a “shallow-bed” (SB) zeolite.

Two samples of each activated zeolite specimen were prepared. One of them was sealed off under vacuum and denoted as dehydrated. The second was rehydrated at room temperature up to about 90% of the saturation value of water adsorption. Some samples were only partially rehydrated.

All $^{27}$Al MAS NMR measurements were carried out at 70.34 MHz using a home-made pulse spectrometer with a superconducting magnet. The rotational frequency of the MAS equipment was 3 kHz. As a reference for chemical shift measurements an aqueous solution of AlCl$_3$ (i.e. containing Al(H$_2$O)$_6^{3+}$) was used. $^1$H NMR measurements or proton intensities were carried out at 90 MHz using a home-made pulse spectrometer with a resistive magnet.

### 3. Results and discussion

The quadrupole interaction broadens the central line of the $^{27}$Al NMR signal of the samples under study. The calculation of van Vleck’s second moment and a comparison of the linewidth of spinning (MAS) and non-spinning samples show that the influence of dipole–dipole interaction and of the chemical shift anisotropy on the linewidth can be neglected. Therefore, the quadrupole frequency $\nu_Q$ can be determined from the linewidth $\delta \nu_{1/2}$ using the equations

$$\nu_Q^2 = \frac{0.875}{1 + \frac{1}{3} \eta^2} \nu_L \delta \nu_{1/2},$$

or

$$\nu_Q^2 = \frac{3.185}{1 + \frac{1}{3} \eta^2} \nu_L \delta \nu_{1/2}^{\text{MAS}},$$

which are valid for a Gaussian lineshape [9] $\delta \nu_{1/2}$ and $\delta \nu_{1/2}^{\text{MAS}}$ denote the linewidth without and with magic-angle spinning of the sample, respectively. $\nu_L$ is the Larmor frequency and $\eta$ the asymmetry parameter of the electric field gradient. For $\eta$ we use the value of 0.95 as determined by the fitting of the resonance line of the non-activated zeolite CaA measured in the low field at 9 MHz (see e.g. ref. [10]).

The influence of the activation procedure upon the quadrupole frequency, calculated from the linewidth by means of the equations given above, is shown in table 1. The dependence on the water adsorption was investigated for a sample activated under deep-bed conditions up to 300°C (table 2).

Increasing values of the quadrupole frequency correspond to increasing values of the electric field gradient and therefore to a stronger deviation from the cubic symmetry of the AlO$_4$ tetrahedron. As can be seen from table 2, rehydration of a sample leads to lower values of the quadrupole frequency (which corresponds to a reduction of the lattice distortion). However, taking into consideration the value of $\nu_Q =$

### Table 1

<table>
<thead>
<tr>
<th>Temperature of activation (°C)</th>
<th>Quadrupole frequency $\nu_Q$ (kHz)</th>
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<tbody>
<tr>
<td></td>
<td>deep-bed activated</td>
</tr>
<tr>
<td>dehydrat. rehydrat.</td>
<td>dehydrat. rehydrat.</td>
</tr>
<tr>
<td>20</td>
<td>440</td>
</tr>
<tr>
<td>100</td>
<td>510</td>
</tr>
<tr>
<td>200</td>
<td>630</td>
</tr>
<tr>
<td>300</td>
<td>700</td>
</tr>
<tr>
<td>400</td>
<td>730</td>
</tr>
<tr>
<td>500</td>
<td>750</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Number of H$_2$O molecules per cavity</th>
<th>$\nu_Q$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>700</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
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<tr>
<td>7</td>
<td>620</td>
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<tr>
<td>17</td>
<td>580</td>
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<td>32</td>
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been observed in the $^{27}$Al MAS NMR spectra of rehydrated zeolites HY [4] could not be found here. However, an additional signal appears at the position of 79 ± 1 ppm. Taking into account the quadrupole correction (cf. ref. [9]) the chemical shift of this additional signal is 81 ± 1 ppm.

According to refs. [11,12] a signal with a chemical shift of 80 ppm must be ascribed to the anion $\text{Al(OH)}_4^-$ of aluminates (for instance $\text{Na(Al(OH)}_4$). Therefore the abovementioned experimental results of the $^{27}$Al MAS NMR measurements can be explained as follows: Extra-lattice aluminium is dissolved in acidic environments by forming $\text{Al(H}_2\text{O)}_p^3^+$ cations (zeolite HY) and in a basic environment by forming $\text{Al(OH)}_4^-$ anions (zeolite CaA). The signal assigned to the aluminate anion was observed in CaA samples activated at temperatures from 200°C up to 500°C under deep-bed conditions followed by a rehydration. Samples prepared under shallow-bed conditions or deep-bed treated dehydrated zeolites CaA show no signal at this position.

Table 3 gives the number of aluminate anions per pseudo-unit cell, i.e. per cavity. The calculation of these values is based on the assumption of 12 aluminium atoms per cavity. The relatively high values for the only partially rehydrated samples can be explained by the higher pH value in the partially hydrated zeolites (in comparison with the fully hydrated samples). The results in table 3 show that after a 300°C deep-bed activation, more than 1.8 aluminium atoms per cavity are released from the zeolite lattice.

$^1$H NMR measurements of the intensity of OH groups yield 3.0 ± 0.3 OH groups per cavity for both dehydrated and rehydrated 300°C deep-bed activated samples and 1.1 ± 0.3 OH groups for the 400°C shallow-bed activated samples. The higher value for the deep-bed activated samples supports the assumption.

Table 3
Number of aluminate anions per cavity for deep-bed activated samples of zeolite CaA: Fully rehydrated and only partially rehydrated (6 H$_2$O molecules per cavity)

<table>
<thead>
<tr>
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<th>Fully rehydrated</th>
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<tbody>
<tr>
<td></td>
<td>200°C DB</td>
</tr>
<tr>
<td>number of aluminate anions per cavity</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>300°C DB</td>
</tr>
<tr>
<td>number of aluminate anions per cavity</td>
<td></td>
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</table>

Fig. 1. $^{27}$Al MAS NMR spectra measured at 70 MHz of zeolite CaA; (a) 200°C deep-bed activated and fully rehydrated; (b) 300°C deep-bed activated and partially (6 H$_2$O per cavity) rehydrated.
of the formation of aluminate anions. Detailed \(^1\)H NMR studies are in progress.

A zeolite NaA (activated at 300°C under deep-bed conditions and rehydrated) provides no signal of extra-lattice aluminium. This fact agrees well with the statement of Pluth and Smith [13] that reflexes corresponding to aluminium in the sodalite unit could not be observed for zeolite NaA. Pluth and Smith [7] found in a sample of CaA, heated up to 350°C in a treatment similar to a deep-bed activation, 0.3 Al complexes in the centre of the sodalite unit. De Roy and Vasant [14] observed a reflex related to the centre of the sodalite unit at an activation temperature of 150°C but not at lower temperatures.

Extra-lattice aluminium species in the supercage are difficult to detect by X-ray diffraction, because an irregular arrangement of these species must be assumed. The number of aluminate anions per cavity measured in the present work is the minimum number of extra-lattice aluminium atoms. The maximum number of extra-lattice aluminium cannot exceed two aluminium atoms per cavity since a greater deficiency of lattice aluminium should be observable by X-ray diffraction measurements or by a decrease of the intensity of the line at 50 ppm in the \(^{27}\)Al MAS NMR spectra.

4. Conclusions

During a deep-bed activation of the zeolite Ca\(_{4,2}\)Na\(_{3,6}\)A above 200°C, about 2 aluminium atoms per cavity are released from framework positions. This aluminium exists in the dehydrated zeolite as some kind of aluminium oxide. After rehydration some of the extra-lattice aluminium forms aluminate anions, with greater efficiency for only partial rehydration. With increasing temperature of activation a decreasing amount of extra-lattice aluminium is able to form aluminate anions during rehydration of the sample.

References